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FEASIBILITY STUDY FOR THE DEVELOPMENT OF A MULTIFUNCTIONAL EMISSION DETECTOR FOR AIR POLLUTANTS BASED ON HOMOGENEOUS CHEMILUMINESCENT GAS PHASE REACTIONS

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AeroChem Research Laboratories, Incorporated
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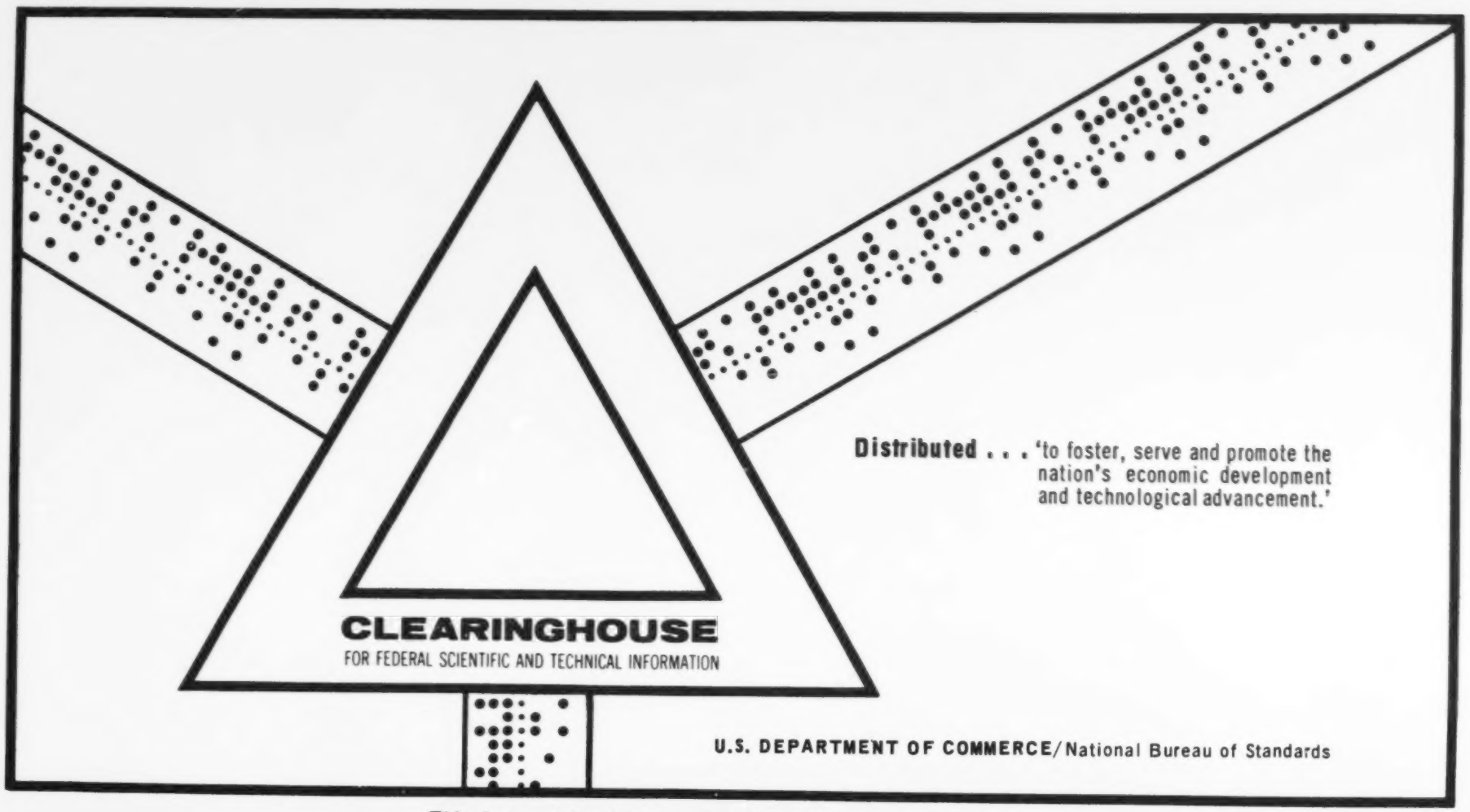

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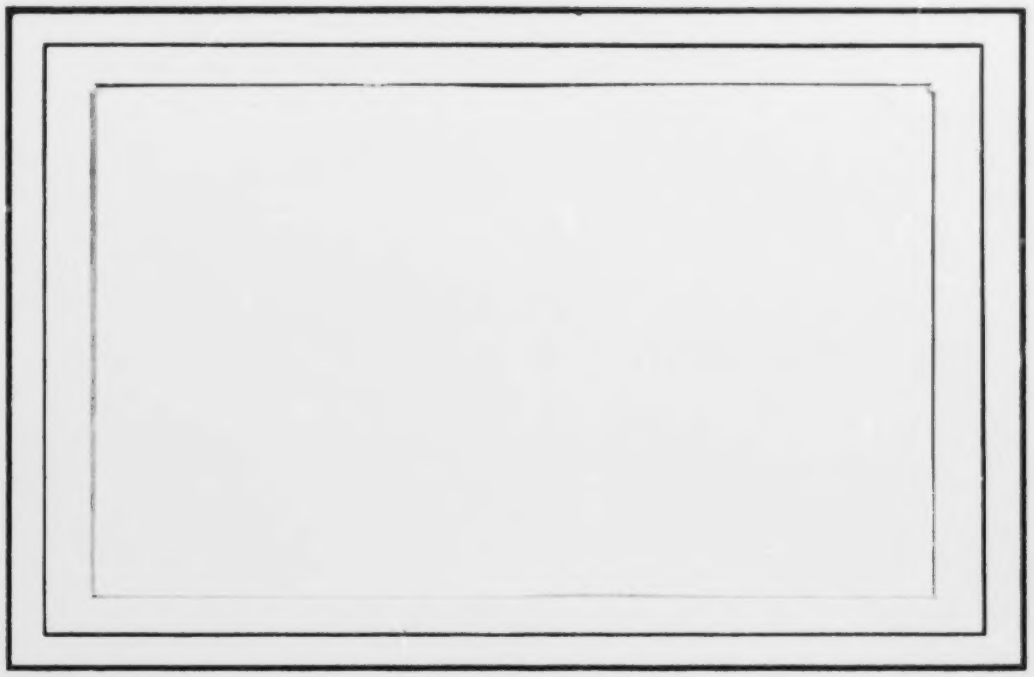

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SYBRON CORPORATION

Princeton, New Jersey

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SUMMARY

The reactions of common air pollutants, such as NO, NO_2, and CO, with certain second reactants, such as ozone or O atoms, result in light emission. Measurements of the emission intensity can be used to determine the concentration of the pollutants. In a detector based on this principle, ambient air and the second reactant can be continuously flown through and mixed in a reactor under moderate vacuum. After calibration a continuous record of pollutant concentration can be obtained. Specific sensitivity to a given pollutant is obtained by a suitable choice of the second reactant and a light filter.

To demonstrate the feasibility of the method, the detection of NO using O_3 has been studied experimentally. A linear response from about 4 ppb NO to at least 100 ppm NO is obtained. NO_2, CO_2, CO, C_2H_4, NH_3, SO_2 and H_2O in concentrations found in polluted air do not interfere with NO monitoring. Based on these results and data for other chemiluminescent reactions, it is shown that homogeneous chemiluminescence monitors for O_3, $NO_x = NO + NO_2$ and CO can probably also be developed.

A comparison of various methods of photomultiplier tube output measurement has been made. Though the ultimate sensitivity of lock-in amplification methods may be higher, inexpensive dc measurement techniques appear adequate for monitoring of pollutants over the full range of concentrations of interest in air quality control.

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I. INTRODUCTION

The homogeneous gas phase reactions of common air pollutants, such as NO, NO_2 and CO, with certain second reactants, such as ozone or O atoms, are known to result in light emission. These reactions have usually been studied in continuous flow reactors. Measurement of the light intensity of the reactions occurring when the pollutants are mixed with a large excess† of the second reactant should in principle be a suitable method for continuous monitoring of pollutants. A priori calculations based on the published spectral distribution of the light emitted, the rate constants for light emission and the response characteristics of photomultiplier tubes, indicated that the light intensity would be quite adequate for monitoring of pollutants over the concentration ranges of interest.

The suggested use of homogeneous gas phase chemiluminescent reactions for monitoring purposes appears attractive for a number of reasons, particularly:

1. The emissions are specific for the pollutant being monitored; suitable choice of a light filter and the second reactant should allow interference-free measurements.
2. The chemiluminescent light intensities from homogeneous gas-phase reactions in continuous flow systems are rather insensitive to changes in surface properties.
3. A family of chemiluminescence monitors may be constructed, each unit of which is specific for one pollutant, but all of which are similar in operation. The convenience in the operation of monitoring stations of families of instruments with similar manipulation and maintenance requirements would be considerable.

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† A large excess of second reactant is needed so that its concentration is not measurably affected by the pollutants.

A schematic design for a chemiluminescence detector is shown in Fig. 1. The air to be monitored and the second reactant, e.g., ozone, enter the reaction vessel through separate inlets. Rapid mixing occurs and a chemiluminescent reaction takes place. A preset flow of the gases is maintained by a mechanical vacuum pump. The pressure in the reaction vessel is typically 1 Torr and the size of the vessel 1 liter. The intensity of the light emitted is measured by a photomultiplier tube and associated read-out devices (current meter and recorder). After calibration with samples of known concentration, a continuous record of the concentration of the pollutant in air can be obtained.

To demonstrate the feasibility of the method and to determine optimum operation conditions, an experimental monitoring system has been built and incorporated in an apparatus which allows for convenient change in flow rates and pressure. Our studies with this device have concentrated on the detection of NO, using O_3 as the second reactant; the lack of interference by other common air constituents and pollutants with the response of the NO/O_3 system has been established. To arrive at conclusions regarding the cost of equipment necessary for various monitoring requirements, a comparison has also been made between various methods (ac and dc) of measurement of the light signals generated.

II. EXPERIMENTAL

A. Flow System

A schematic of the Pyrex/stainless steel/copper flow system is shown in Fig. 2. Oxygen (Linde Aviators Breathing Grade) and Nitrogen (Matheson, Prepurified), dried near atmospheric pressure by activated alumina, pass through flow meters and needle valves into the low pressure part of the system. On the high pressure side the oxygen is ozonated ($\approx 0.5\%$)† by a photolytic

† Relative concentrations in this report are expressed on a molar basis (v/v).

ozonator (OREC Model 03VI).† Nitrogen serves as the carrier gas for NO and the other pollutants for which possible interference with NO detection was investigated. The NO is introduced into a 3 liter spherical Pyrex exponential dilution flask, containing a completely enclosed magnetically-driven stirrer. The O_2/O_3 and N_2/pollutant streams are mixed in the 1 liter spherical Pyrex reactor. The flow is maintained with a 5 CFM Welch Duo-Seal vacuum pump.

The gas streams enter the reaction flask through nozzles having small openings (1 to 2 mm diam) in the direction perpendicular to the neck of the flask. The reactor has a 7.5 cm diam flat quartz window facing the photocathode of the photomultiplier tube used for light intensity measurements. The reactor is coated externally with Eastman white reflectance paint ($BaSO_4$) and is packed with MgO powder inside an aluminum box. The use of this powder further increases the available light intensity and provides for a light-tight detection system.

B. Procedure

The experiments were performed at room temperature at the following reactant concentrations (in moles liter^{-1}): $[N_2] = 2.7 \times 10^{-5}$; $[O_2] = 2.7 \times 10^{-5}$; $[O_3] = 1.1 \times 10^{-7}$. Total reaction pressure was held at 1 Torr‡ ($[M] = 5.4 \times 10^{-5}$ mole l^{-1}). The flow rates of O_2 and N_2 into the system were 1.25 ml (STP) sec^{-1}. The ozone flow was measured by iodometric titration. A visual check

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† Higher ozone concentrations can be obtained from electrical discharges than from common photolytic methods. However, a photolytic ozonator is to be preferred for the present application since electrical discharges tend to produce NO, even when N_2 is present only as a minor impurity in O_2.

‡ This pressure was chosen because at higher pressures (≈ 3 Torr) mixing became unsatisfactory, while pressures below about 0.5 Torr could not be maintained at convenient flow rates with the 5 CFM pump.

of mixing conditions was performed.† The results obtained in Section III. B confirm that mixing conditions were satisfactory.

Nitric oxide concentrations were varied over a range of 4 ppb to 100 ppm of that of N_2 (1.1×10^{-13} to 3×10^{-9} mole l^{-1}). The NO was purified by passage over (i) activated alumina (for removal of H_2O) and (ii) Ascarite (for removal of NO_2). Atmospheric pressure samples were injected with a gas-tight syringe through the rubber stopper of a 5 liter Pyrex predilution flask, containing prepurified N_2 at atmospheric pressure. After thorough mixing, samples containing NO in concentrations in the range of 10 to 10^5 ppm were taken from this flask and injected through the rubber stopper injection port of the exponential dilution flask of the main flow system, see Fig. 2. An exponential dilution flask is a stirred flask purged at a constant volume flow rate. Under these conditions the concentration of a sample injected in the flask decreases exponentially[1]:

$$C = C_0 \exp(-Qt/V) \qquad (A)$$

where, C_0 = Initial concentration

Q = Volume flow rate at the flask pressure

V = Effective volume of the dilution flask

t = Time elapsed from start of dilution.

The pressure in the flask was maintained at 50 Torr, which gives a convenient

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† For the visual tests, the O_2/O_3 stream was replaced by an O_2/O stream, obtained by subjecting the O_2 stream to a microwave discharge (powered by a Raytheon 125 Watt microwave generator), rather than to the ozonator lamp. O atoms were used in these visualization experiments since a major portion of the emission of the NO/O reaction is in the visible part of the spectrum, while NO/O_3 emission is not visible, cf. Section III. A.

time constant (V/Q on the order of 150 sec) for our measurements.† Some typical dilution curves are shown in Fig. 3. The recorder gives a continuous record of the system response; the points shown on the dilution plots are from these continuous records.

In a number of experiments the effect of the presence of other air constituents and pollutants on the detector response to NO was investigated. Best regular grade gases were used. CO_2, SO_2, C_2H_4 and NH_3 were taken directly from cylinders. CO was first passed through a liquid N_2 trap for removal of carbonyl compounds. NO_2 was taken from a blackened Pyrex flask in which it had been mixed with an equal portion of atmospheric air; this procedure was followed to oxidize trace amounts of NO to NO_2 and to prevent photodissociation of NO_2. These interference gases were injected in the same exponential dilution flask as used for NO. Separate predilution flasks were used. In early experiments with NO_2 this gas was injected through the port marked "H_2O" in Fig. 2, using a second N_2 flow system similar to that shown in Fig. 2. This procedure gave results identical to those obtained with the single N_2 flow system.

Water vapor also could be introduced with a second N_2 flow system. Up to 75% of the total N_2 flow was diverted through this system, which was designed so that N_2 either passed through a saturator or directly to the "H_2O port." This set-up allowed for rapid comparison between the detector response to NO with 75% saturated and dry N_2. The saturator was filled with H_2O at 45°C. Complete saturation of N_2 flowing through the H_2O port was achieved, as evidenced by the formation of water droplets in a room temperature trap, downstream from the saturator.

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† The effective volume of the flask has to be determined experimentally. In our experiments it was found to be on the order of 2500 ml and somewhat dependent on stirring rate. Therefore, Eq. A was useful mainly for planning our experiments but could not be relied upon to calculate concentrations flowing into the reactor. See further, Sections II. D and III. B.

C. Light Detection System

The radiation from the reactor is filtered through a Corning CS 2-60 filter, cutting off radiation of $\lambda < 6100$ Å (see further Section III. A); its intensity is measured with an EMI 9558 QA trialkali photomultiplier tube. This model was selected because of its relatively high sensitivity in the 6000 - 8750 A region, good signal-to-noise ratio (S/N) characteristics and its usefulness over a wide range of wavelengths. The spectral response characteristic of the tube (S20) is shown in Fig. 4. The tube is contained in a Products for Research TE-104 thermoelectrically-cooled housing and maintained at about -20°C, at which temperature an S/N some 3 orders of magnitude higher than at room temperature is obtained.[2] The cathode-to-anode voltage of 1400 V is supplied by a Pacific Photometric Instruments Model 200 power supply. The tube output is measured by a Keithley Model 602 solid state electrometer--to which is added a home-built dc zero-offset device--and recorded with a Heath EU-20B Servo-recorder.

The above direct current measurement arrangement was selected as a result of a number of preliminary experiments in which a comparison was made between the sensitivity of this method and that available from phase-sensitive amplifiers. Two such amplifiers were used: A versatile, high-sensitivity model (Princeton Applied Research HR-8) and a relatively inexpensive type (PAR Model 120). To provide the modulation for these ac amplifiers, a Brower Model 312 CM light chopper was placed in front of the photocathode. This chopper has a 2-aperture 11 inch diam steel blade and was used to provide a 100 Hz signal. The reference signal is generated by a proximity switch facing the chopper blade. For NO detection under the conditions described above we found the respective noise levels to correspond approximately to:

Keithley electrometer:	4 ppb NO
PAR Model HR 8 lock-in amplifier:	1 ppb NO
PAR Model 120 lock-in amplifier with Model 112 pre-amplifier:	10 ppb NO

Further improvement in the response of the HR-8 could probably have been

achieved by the use of an ac zero-offset device (Model 123) made by PAR for this lock-in amplifier. In view of the satisfactory relative response of the electrometer there appeared to be no need for obtaining this device, although in its absence we were unable to off-set (with the HR-8) the background signal due to impurities in the ozone source. The signal generated by this source was the equivalent of about 5 ppb of NO. Since we did have a zero off-set on the electrometer, its use was preferred. Moreover, for an ultimate practical air pollutant detector the use of a dc current measurement method implies a much lower cost than achievable with a lock-in amplifier/chopper method. Since the currents generated by 4 ppb NO are on the order of 10^{-9} A (see below), a dc current measuring device less sensitive and less expensive than an electrometer can be used in a practical unit.

D. Experience Gained from Preliminary Experiments

In this section we discuss results from preliminary experiments which aided in the design of the final experiments and may be useful for future reference.

Reaction Vessel - Initially two Pyrex multihole nozzles were used in which the holes had been punched with a hot tungsten wire. O_3 destruction occurred at the nozzle openings. A glass-blown single hole ($\approx$ 2 mm diam) ozone nozzle was therefore used. Apparently satisfactory mixing conditions in the reaction vessel were obtained when this nozzle was combined with a multihole nozzle for the N_2/pollutant inlet, and both nozzles faced each other in the neck of the flask.

The light intensity from the NO/O_3 reaction was measured in a 2.2 cm i.d., 14 cm long cylinder (for end-on observation), a 1 liter sphere and a 5 liter sphere. All these reaction vessels were of Pyrex glass externally covered by aluminum foil. The highest S/N was obtained with the 1 liter sphere, which was therefore selected.

Temperature variation over the range 20 to 200°C was investigated by heating the reaction vessel. Heating to 50°C had no appreciable effect on S/N, but higher temperatures adversely affected S/N due to increased radiation from the vessel walls.

Exponential Dilution Flasks - Figure 3 shows a typical exponential dilution plot. The concentration vs. time curves obtained with these flasks showed, independent of the magnitude of the initial pollutant concentration, an exponential concentration decrease for about two to three orders of magnitude, after which the concentration drops less rapidly. A similar behavior has been observed by previous investigators.[3] This levelling-out of the decay curves can apparently be attributed either to gases absorbed on the walls that are slowly released or gas pockets that are ineffectively stirred. These deviations caused but minor inconvenience since we could cover any range of pollutant concentrations of interest by using a number of injections at different initial concentrations, $[NO]_0$, less than two orders of magnitude apart. Nonetheless, we made a number of experiments to see whether the linear range of one exponential dilution run could conveniently be increased. Thus the volume of the flask was varied from 1 to 5 liter, a "Lif-O-Gen" GLX40 steel sphere was used instead of a Pyrex sphere, several stirrers were used, the dilution pressure was changed from 10 to 100 Torr and the flasks were heated to 200°C. None of these changes extended the linear range significantly and the heating actually had a deleterious effect.

Light Choppers - We originally ordered a light chopper, cooled PM housing and lock-in amplifier from one source (Princeton Applied Research Corporation). However, the housing obtained (made by Products for Research) did not fit over the chopper motor. As a result, the housing had to be moved some 10 cm away from the reaction vessel; because of the inverse square law effect, this resulted in unnecessary losses in light intensity. We then obtained a Brower 312 CM chopper which allowed the phototube housing to come within about 2 cm of the reaction flask. Several chopper blades have been used (with the Brower unit).

The best results (one order of magnitude larger S/N than with the PAR chopper) were obtained with the 2-aperture, 11 inch diam blade. Over the range 5 to 300 Hz, no dependence of S/N on chopping frequency was found to exist (as long as multiples of 60 Hz are avoided). In the initial experiments with the Brower chopper, it was established that the external reference light signal used in this unit generated negative signals which made it nearly impossible to measure NO concentrations below about 100 ppb. Therefore, the chopper was returned to the factory for modification. The reference signal in the modified unit is provided by a proximity switch activated by the steel chopper blade; this unit operates completely satisfactorily, and was retained.

Photomultiplier Tube and Tube Housing - The original socket delivered with the cooled housing placed the photocathode 2.5 cm further away than necessary from the window of the housing, and hence the reaction flask. A modified socket, which placed the photocathode 2.5 cm closer to the window, was used for the final experiments. However, there was no appreciable difference in S/N obtained with the two sockets.

Variation of the photomultiplier tube voltage showed that the highest values of S/N were obtained at about 1400 V.

The manufacturer (EMI) supplies a doughnut-shaped permanent magnet to be mounted in front of the photocathode for increased S/N.[2] However, this magnet actually decreased S/N. This was due to the fact that the noise level of the cooled phototube hardly changed, but the signal decreased appreciably (probably due to the reduced aperture).

III. RESULTS AND DISCUSSION

A. The Reaction Between NO and O_3

On the basis of the available literature, ozone was selected as a suitable second reactant for NO monitoring. Other reactants, such as O and H atoms, also produce a rather intense chemiluminescence[4, 5] with NO; however, they also

react rapidly[6, 7] with NO_2, producing NO. As a result, these atoms are suitable for the determination of $[NO] + [NO_2]$, but not for that of $[NO]$. The slow reaction of NO_2 with O_3 generates only higher oxides (NO_3, N_2O_5).[8, 9]

The reaction between NO and O_3 has been investigated extensively by Thrush et al.[10, 11] The chemiluminescence is due to:

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (1a)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (1b)$$

The light intensity, I_1, is given by

$$I_1 = 12 \left\{ \exp(-4180 \pm 300)/RT \right\} \left\{ [NO][O_3]/[M] \right\} \ sec^{-1} \qquad (B)$$

for the 6000 to 8750 Å region for M = air.† The $[M]$ appears in the denominator because the emitting species, NO_2^*, is quenched by M, i.e., any gaseous species present. The relative intensity distribution of the emission spectrum is shown in Fig. 5. It may be seen that no light is emitted below about 6000 Å. Comparison to the EMI 9558 QA phototube spectral response characteristic, Fig. 4, shows that the tube's peak sensitivity falls at wavelengths shorter than 6000 Å. Therefore the use of the CS 2-60 filter does not appreciably interfere with the sensitivity of the monitor for NO detection by O_3, but decreases the possibility of interference by other pollutants. It may also be seen from Fig. 4 that the phototube response cuts off near 8750 Å. Therefore, the I_1 value given by Eq. B is roughly that for the useful emission region of our experiments.

The rate constant for the overall reaction, as defined by

$$-\frac{d[O_3]}{dt} = -\frac{d[NO]}{dt} = k[NO][O_3], \qquad (C)$$

is 1×10^7 l mole^{-1} sec^{-1} at room temperature.[10] This number is sufficiently small to make consumption of NO by O_3 in the reaction flask essentially

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† The units of I_1 obtained from Eq. B are, for example, Einsteins l^{-1} sec^{-1} or quanta ml^{-1} sec^{-1}, depending on whether mole l^{-1} or number of particles ml^{-1} concentration units are employed.

negligible ($\approx 6\%$) under our operating conditions (residence time ≈ 0.5 sec; $[O_3] = 1.1 \times 10^{-7}$ mole l^{-1}). The absence of an appreciable change in reactant concentration is a necessary prerequisite for a uniform light intensity in the reactor, needed to obtain a linear response from the detector.

B. Linearity of Response and Limit of Sensitivity for NO Detection

Figure 6 gives a composite plot of the detector response to NO. It may be seen (i) that the light intensity varies linearly with NO concentration over the range of concentrations investigated ($\approx$ 4 ppb to 100 ppm), and (ii) that 4 ppb represents the approximate limit of sensitivity when a dc detection method (electrometer) is used. The data were taken under identical operating conditions. Two types of data points may be distinguished, (i) those obtained from the initial injection of NO into the dilution flask and (ii) points taken from exponential dilution plots, cf. Fig. 3, on the assumption that a decrease in intensity by a factor x corresponds to a decrease in NO concentration by a factor x. It may be seen that both types of points fall along the same line, thus confirming the linearity of response with respect to NO concentration. The scatter in the data of Fig. 6 increases with decreasing NO concentration. This can reasonably be attributed to a decreasing accuracy of sample preparation.

The range of concentrations of NO encountered in (and of interest to) air quality control falls within the limits[12] 10 ppb to 1 ppm. The linearity of response and sensitivity of the detector thus appear quite satisfactory for its use as a monitor of NO in air.

C. Effect of Other Air Constituents on the Detector Response to NO

The possibility of interference by other commonly encountered air pollutants/constituents was investigated by adding them to the N_2/NO flow. These constituents and the minimum concentrations in which they were to be tested were selected in consultation with the NAPCA contracting officer, R. K. Stevens. A typical test run is shown in Fig. 7 for the case of NO_2. This figure shows points obtained (i) in a normal NO dilution run and (ii) an NO run during which NO_2 was injected. Since the concentration of NO_2 decreased in the

dilution process (presumably at the same rate as that of NO) it was desirable to repeat the NO_2 injections several times in the course of one NO run. It may be seen from this figure that the presence of 9 ppm NO_2 does not influence the detector's response to NO down to about 6 ppb. The same procedure as for NO_2 was followed for CO_2, CO, C_2H_4, NH_3 and SO_2. The results are summarized in Table I in terms of concentration of the constituent tested which was found not to interfere with the nitric oxide signal at $[NO] \leq 10$ ppb. It may be seen that these concentrations are at least equal--and in most cases considerably higher--than typical high concentrations of these compounds in polluted air. By using concentrations of NO_2, C_2H_4 and NH_3 about two times higher than given in the last column of Table I, signals in excess of those obtained at 10 ppb of NO were observed. For the other compounds this column gives the highest concentrations tested.

The H_2O data were obtained in a different manner. They pertain to a comparison between streams of N_2/NO (i) dried and (ii) 75% saturated with water; no difference was observed in signals from these streams. With the experimental set-up employed, we could not use a 100% saturated stream (some of the NO would have been absorbed in the water of the saturator). However, it appears very unlikely that any major interference could occur due to the fractional increase in $[H_2O]$ represented by the increased saturation.

D. Monitoring of O_3, $NO_x = NO + NO_2$ and CO

A major advantage accruing to the application of homogeneous chemiluminescent reactions for monitoring of air pollutants would be the use of a set of similar instruments for a number of pollutants. One can obtain an idea of the likelihood of obtaining such multifunctional detectors by discussing a few examples. This is done here by using the experimental data obtained in the present work and published spectral distributions and rate constants for light emission of a number of chemiluminescent reactions.

TABLE I

LACK OF INTERFERENCE OF OTHER AIR CONSTITUENTS WITH NITRIC OXIDE MONITORING BY OZONE

Constituent	Typical High Concentration Encountered in Air Pollution Monitoring† (ppm)	Concentration Used at which no Interference Was Detected at [NO] ≤ 10 ppb (ppm)
NO_2	0.5	9
CO_2	300	300
CO	25	300
C_2H_4	1	5
NH_3	0.5	9
SO_2	1	25
H_2O	100% saturation	75% saturation

† Data from Stevens,[3] see also Tebbens.[12]

O_3 - The NO/O_3 reaction can also be used to monitor O_3. In this case one would merely replace the O_2/O_3 flow line (Fig. 2) with a carrier gas/NO flow line. The sensitivity of the method at $[NO] = 1.1 \times 10^{-7}$ mole l^{-1} (equal to the O_3 concentration used above) would be the same as that found above for NO, i.e., 4 ppb, and interference effects would also be the same as for NO detection by O_3. The sensitivity could readily be increased by using higher NO concentrations.

$NO_x = NO + NO_2$ - As discussed in Section III. A, in the presence of O atoms NO_2 readily yields NO on a 1:1 basis. The reaction

$$O + NO \rightarrow NO_2 + h\nu \qquad (2)$$

can thus be used to determine $[NO_x]$. The rate constant and spectral distribution of Reaction (2) have been determined by Fontijn, Meyer and Schiff.[4] The light is emitted in a continuum, stretching from 3875 Å well into the infrared. Over the wavelength region for which the 9558 QA tube is sensitive, the rate constant k_2 is about 2.5×10^4 l mole^{-1} sec^{-1}. Oxygen atoms can be generated at the same pressure and flow conditions as used in our NO/O_3 experiments (above), by replacing the ozonator with a microwave discharge, placed on the downstream side of the stopcock D in the O_2 line, Fig. 2. Previous work, e.g., Ref. 4, indicates that under these conditions [O] in the reactor would be about 1×10^{-6} mole l^{-1}. Thus, the light intensity $I_2 = k_2[O][NO] \approx 2.5 \times 10^{-2}[NO]$ sec^{-1}. Using Eq. B of Section III. A, we obtain $I_1 = 1.7 \times 10^{-5}[NO]$ sec^{-1}, for our NO/O_3 experiments.† Hence the sensitivity of the detector as an NO_x detector

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† These data may also be used to calculate the limit of sensitivity of the detector for NO/O_3 emission in terms of quanta detected. The experimental limit of sensitivity is 4 ppb NO, hence $[NO]_{lim} = 4 \times 10^{-9} \times [N_2] = 1.1 \times 10^{-13}$ mole l^{-1} and $I_{lim} = 1.7 \times 10^{-5} \times 1.1 \times 10^{-13}$ Einstein l^{-1} sec^{-1} $= 1.9 \times 10^{-18}$ Einstein l^{-1} sec^{-1} $= 1 \times 10^6$ quanta l^{-1} sec^{-1}.

using O atoms is some 3 orders of magnitude higher than it is as an NO detector using O_3. It actually is somewhat higher yet, since the phototube sensitivity decreases with increasing wavelengths for the spectral region of interest in comparisons of NO/O to NO/O_3 emissions, cf. Fig. 4. It must be recognized that because of the possibility of interference by emissions of reactions of O atoms with other air pollutants, the full spectrum of the NO/O reaction may not be available. However, it appears that even if a relatively narrow wavelength region is selected by the use of an appropriate filter, the sensitivity of the detector for NO_x by O would still exceed that of the NO/O_3 detector.

CO - Carbon monoxide may be monitored by using its reaction with oxygen atoms,

$$CO + O \rightarrow CO_2 + h\nu, \qquad (3)$$

which results in emission of the carbon monoxide flame bands. This banded emission spectrum falls in the 3000 - 5000 Å region, cf. Dixon[13] and Pearse and Gaydon.[14] The rate constant for light emission, k_3, has been determined† by Clyne and Thrush[15] as 1.2×10^1 l mole^{-1} sec^{-1}. Hence at $[O] = 1 \times 10^{-6}$ mole l^{-1}, $I_3 = k_3[O][CO] = 1.2 \times 10^{-5}[CO]$ sec^{-1}. Comparison to our NO/O_3 results gives 6 ppb as the approximate limit of sensitivity. However, the phototube response curve (Fig. 4) shows that in the wavelength region of the CO/O emission, the tube sensitivity is some 5 times higher than in the region of the NO/O_3 emission. This then places the limit of sensitivity at about 1 ppb. Again, interference by other pollutants could in practice result in a higher useful limit.

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† The rate constants for light emission of the NO/O_3 (k_1) and CO/O (k_3) reactions, quoted in this report, were measured by comparison to the NO/O reaction in the same apparatus. The absolute values then were obtained[10, 15] by using the directly measured absolute value for the NO/O reaction.[4] The fact that the intensity ratios used here depend on relative measurements made in the same apparatus enhances their accuracy.

The natural atmospheric background levels of O_3, NO_x and CO are, according to Tebbens,[12] probably approximately 10, 20 and 100 ppb, respectively. It thus appears highly likely that the homogeneous chemiluminescent detector can be used for the monitoring of these pollutants over the full range of their concentrations in polluted air. Of course, experimental confirmation remains desirable. Since the light-emitting reactions are of first order in the pollutant concentration, linear responses can also be predicted.

IV. CONCLUSIONS AND RECOMMENDATIONS

It may be concluded from this study that:

1. It is possible to develop a homogeneous chemiluminescence detector of NO in polluted air which is based on the NO/O_3 reaction and has a linear response from about 4 ppb NO to at least 100 ppm NO.

2. Other common air pollutants and constituents at the concentrations found in polluted air do not interfere with the response of the NO detector.

3. It is highly likely that a homogeneous chemiluminescence detector will be multifunctional. In addition to NO at the least O_3, $NO_x = (NO + NO_2)$ and CO could be monitored with such a device.

To derive practical benefit from this study it is recommended that:

1. An NO monitor based on the NO/O_3 reaction, now be made and tested in the field.

2. Laboratory studies be undertaken to demonstrate the usefulness of homogeneous chemiluminescence detectors for monitoring of other air pollutants, such as O_3, NO_x and CO.

3. Laboratory studies on these other pollutants, if successful, be followed with development and testing of field monitors for these pollutants.

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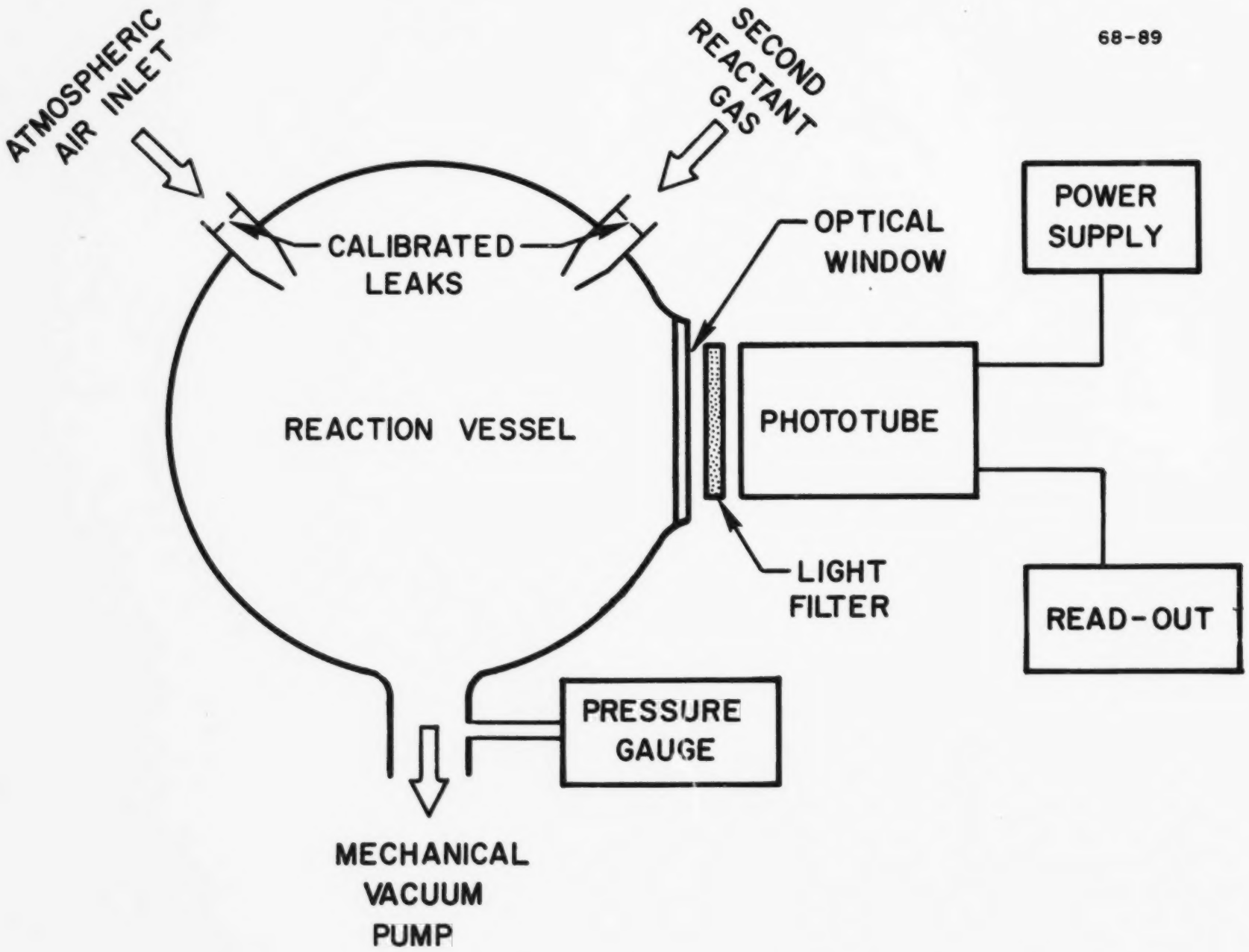

FIG. 1 CHEMILUMINESCENCE DETECTOR

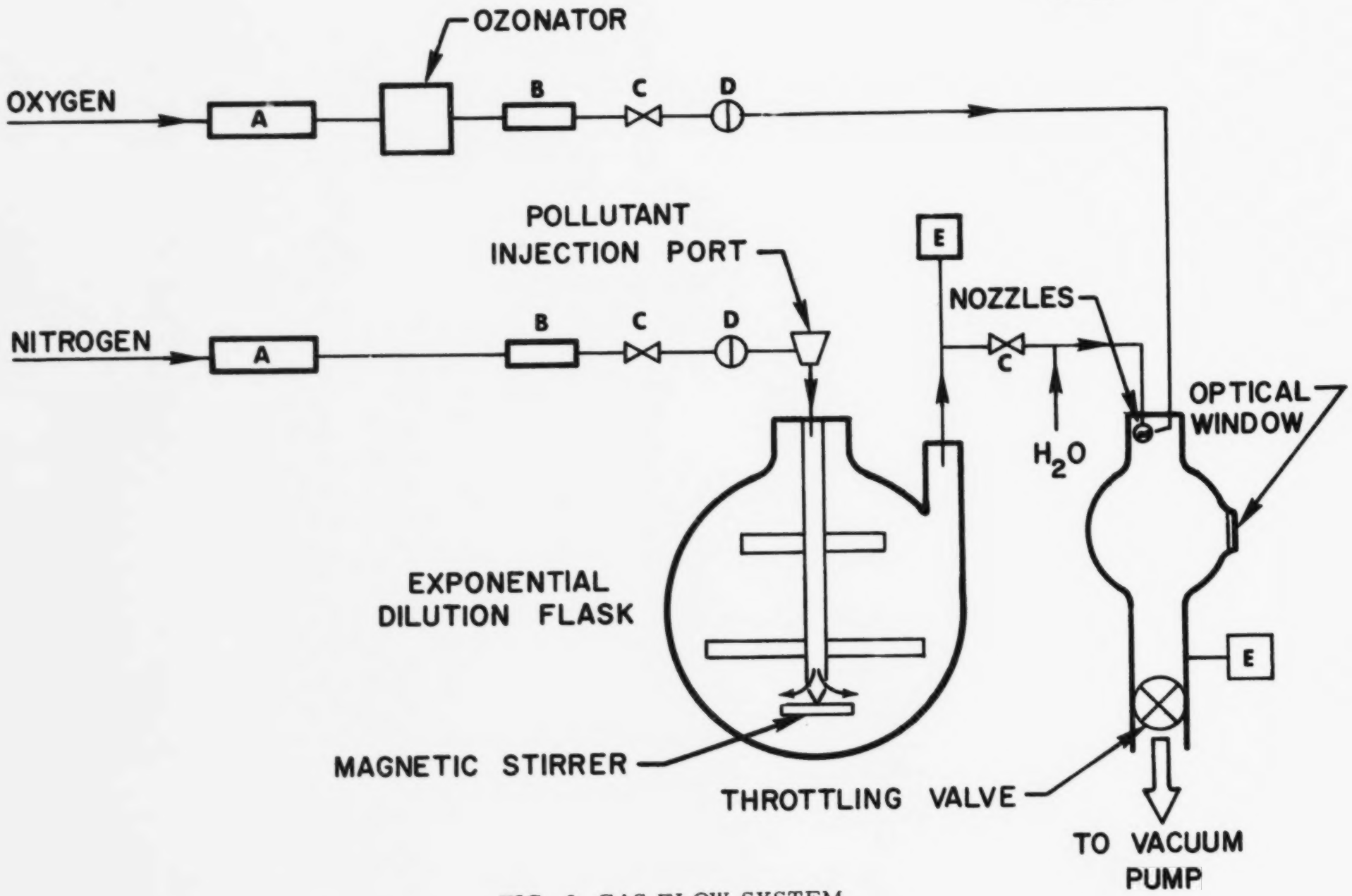

FIG. 2 GAS FLOW SYSTEM

A, absorbing tower; B, flowmeter; C, needle valve;
D, stopcock; E, manometer

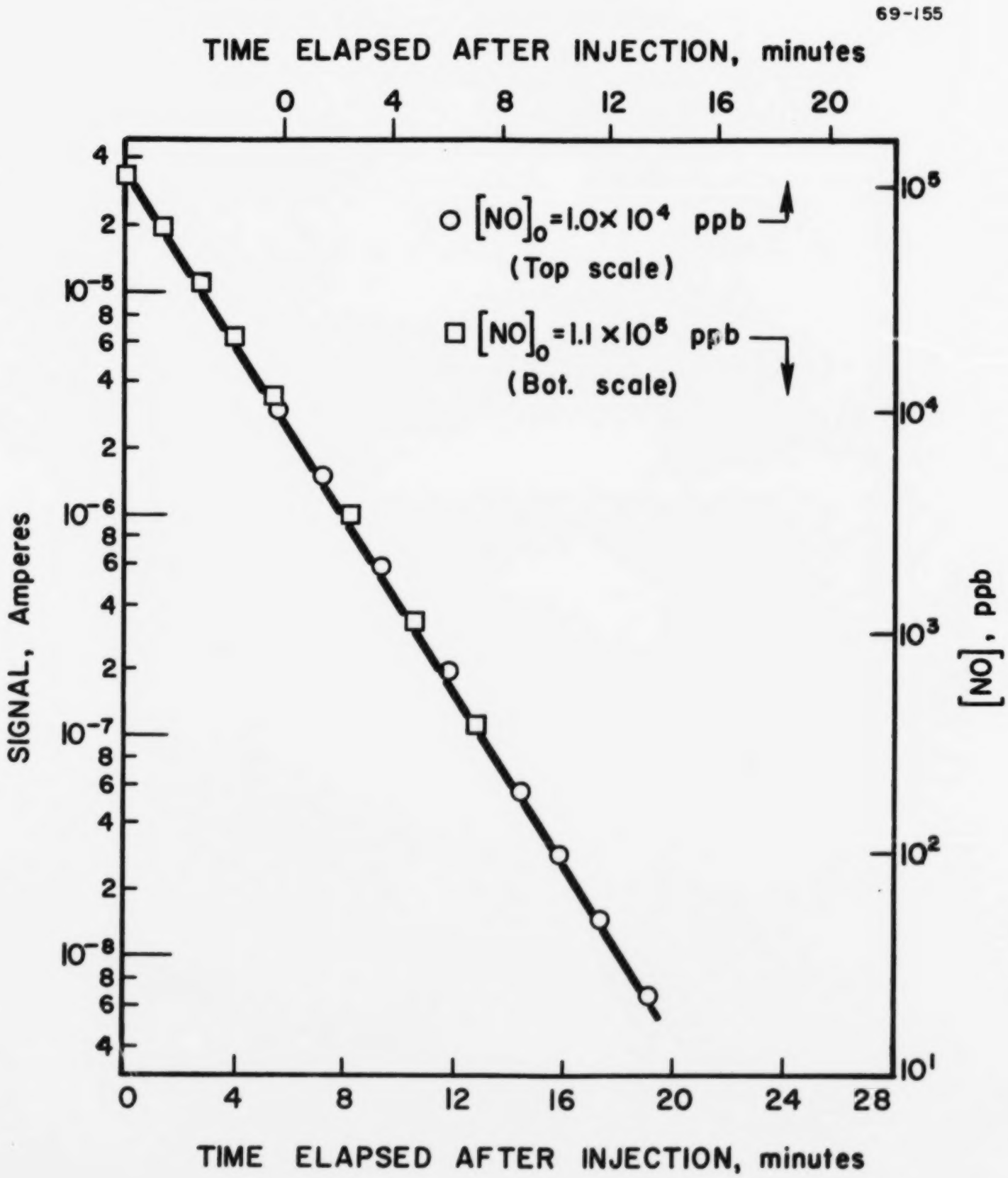

FIG. 3 EXPONENTIAL DILUTION PLOT

69-156

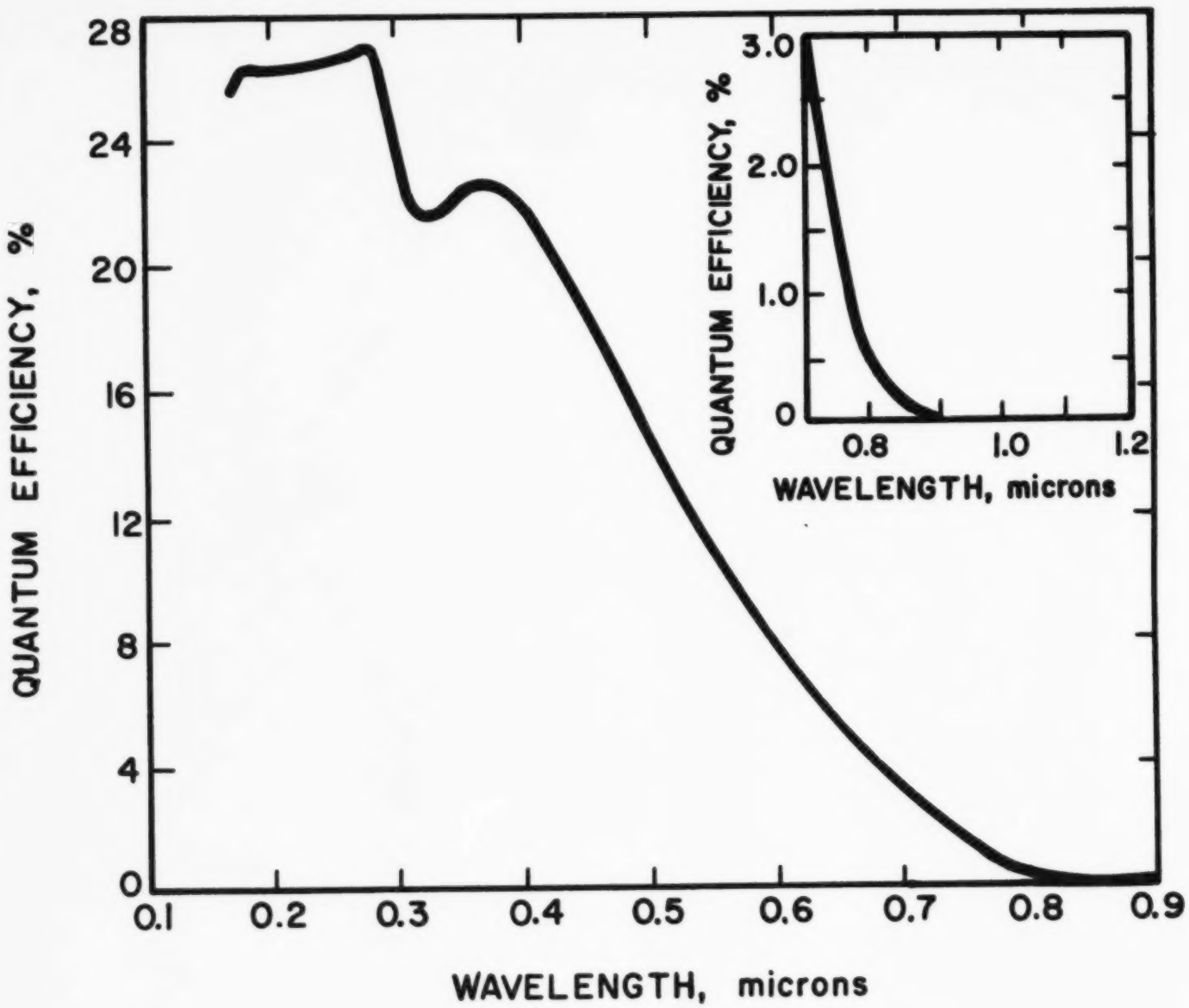

FIG. 4 SPECTRAL RESPONSE OF EMI 9558 QA PHOTOMULTIPLIER TUBE

Manufacturer's data, Ref. 2

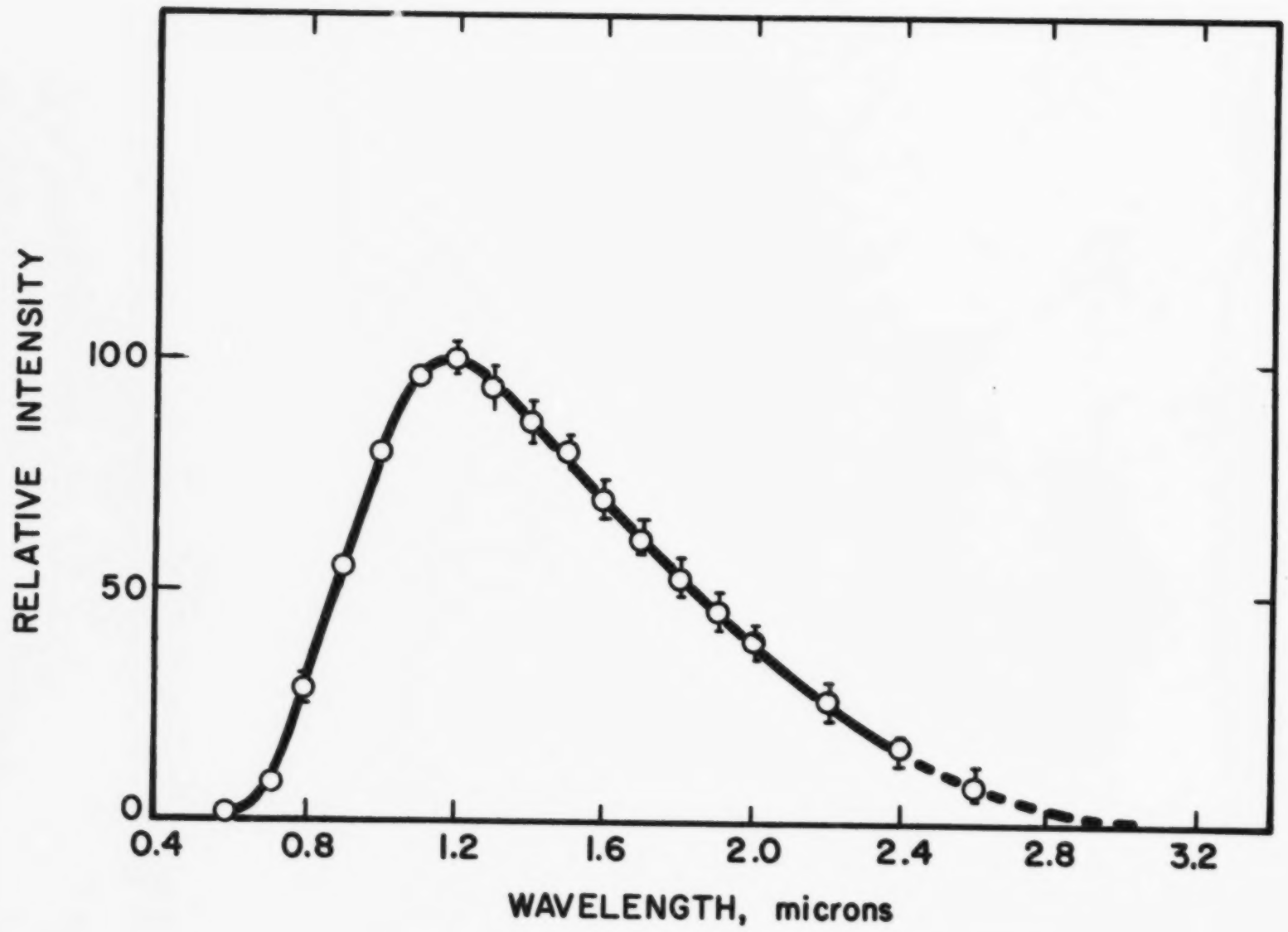

FIG. 5 SPECTRAL DISTRIBUTION OF NO/O_3 EMISSION

Units proportional to quanta per wavelength interval per second. Spectral distribution normalized to Intensity = 100 at $\lambda = 1.2\mu$. Data after Clough and Thrush, Ref. 11.

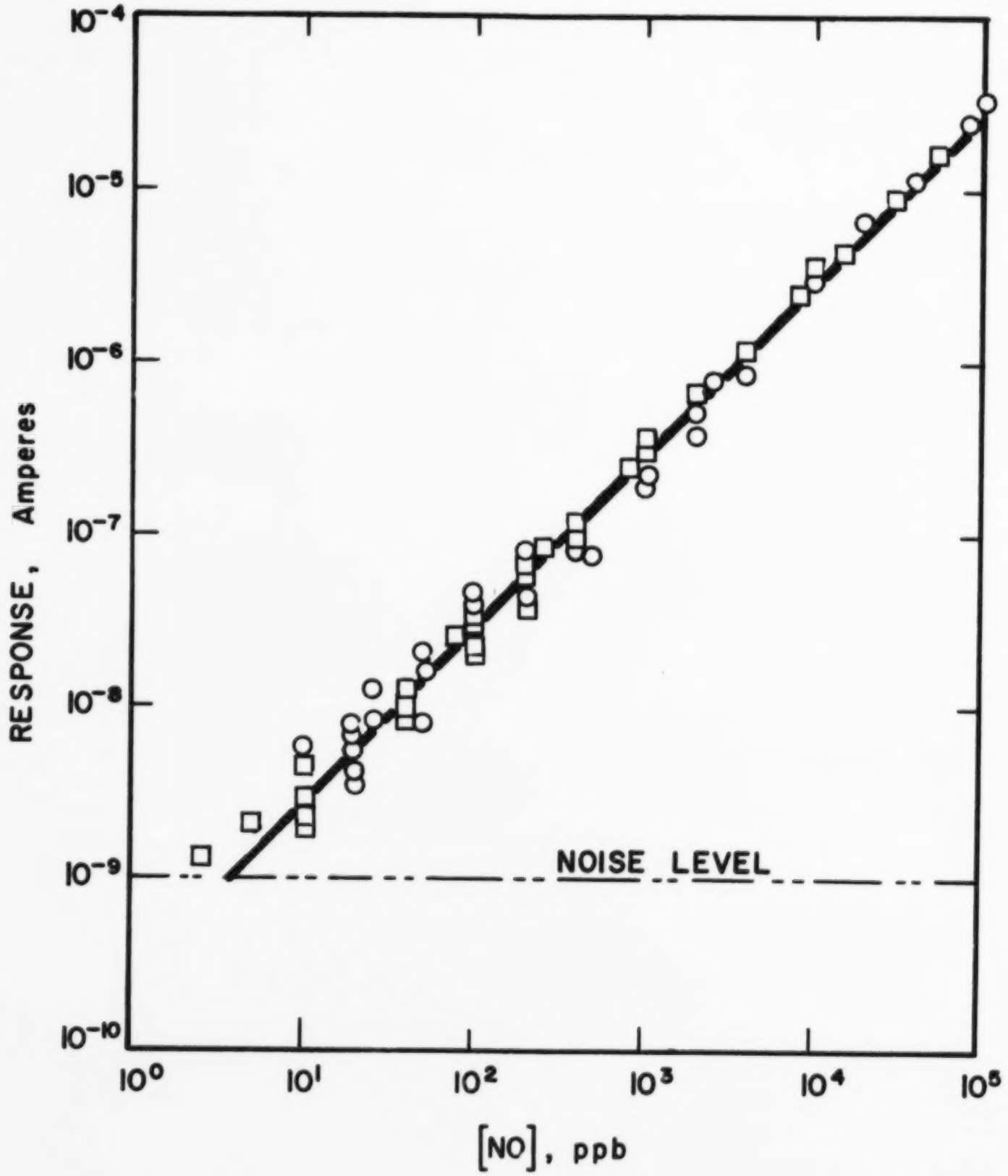

FIG. 6 DEPENDENCE OF THE RESPONSE OF THE CHEMILUMINESCENCE DETECTOR ON NITRIC OXIDE CONCENTRATION

○ = Initial concentrations
□ = Data from exponential dilution plots

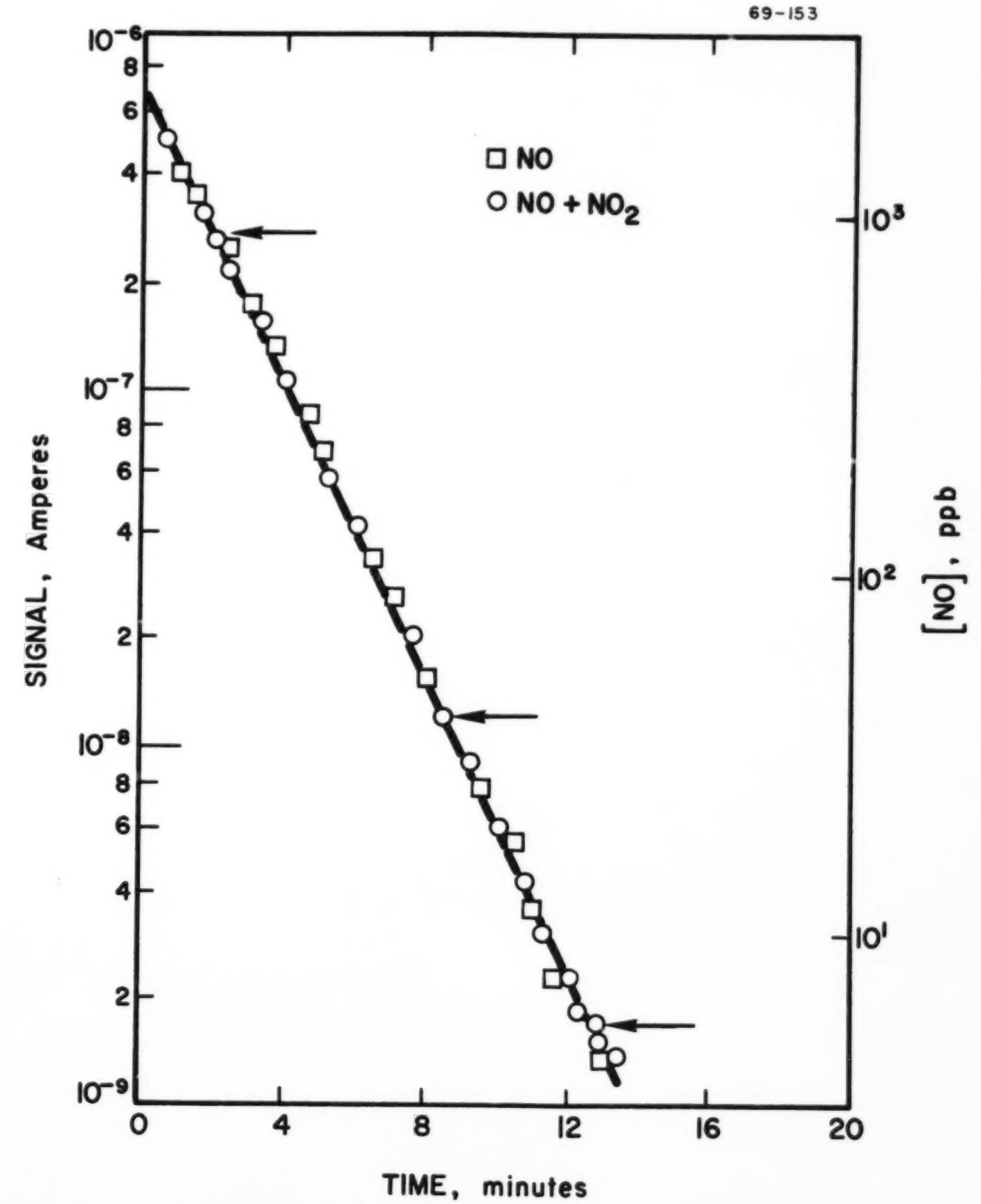

FIG. 7 EFFECT OF NO_2 ON DETECTOR RESPONSE TO NO

The arrows indicate the points at which 9 ppm NO_2 was injected.